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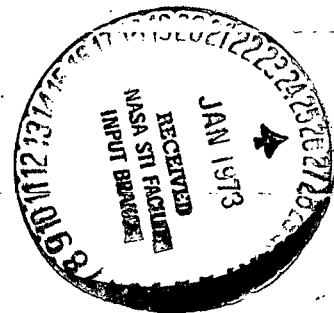
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ADDITION REACTIONS WITH H- AND O-ATOMS AT LOW TEMPERATURES

K. H. Geib and P. Harteck¹

ABSTRACT. Addition reactions are inhibited by creation of a stable compound from another stable compound by increasing the valence of an atom. Preferential addition occurs at low temperatures in compounds in which a secondary valence is created chemically. The familiar final compounds are obtained only through rearrangement of these unstable intermediate compounds.

I. Addition Reaction with Atoms in General

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In a number of reactions, we have seen that atoms can be added to compounds at low temperatures (temperature of liquid air) without significant activation heats [1, 2]. H-atoms are added to oxygen at -190°C and at the temperature of liquid hydrogen instantaneously with formation of a product having the composition H_2O_2 . However, this differs from the familiar hydrogen peroxide in its instability — it begins to decompose at -115° , so that it must be assumed to

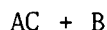
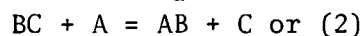
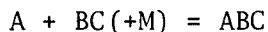
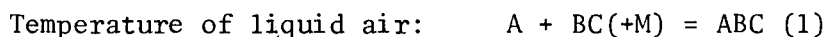
have a different type of bond such as $\begin{array}{c} \text{H} \\ \diagup \\ \text{O}:\text{O} \\ \diagdown \\ \text{H} \end{array}$. Similar unstable compounds include mercuric hydride and the additive compound made up of H-atoms on nitric oxide, HNO or $[\text{HNO}]_n$.

In general, since exchange reactions require an activation heat, the latter are suppressed at low temperatures and the reaction can proceed uniformly as an addition reaction (1) if the latter can take place without activation energy.

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*Numbers in the margin indicate pagination in the foreign text.

At room temperature or above, on the other hand, the activation heats play a less significant role for the exchange reaction and the larger molecules that result from the addition of atoms are broken down again by the same atoms (2). In addition, the raw material may be attacked at room temperature or above (3). Schematically, the reactions in question between an atom A and a molecule BC proceed as follows:



It is a known fact [2, 3] that at room temperature, in gas reactions with atomic hydrogen, the H-atoms in many instances do not have a hydrating effect but a dehydrating one. The exchange reactions are extremely preferred at room temperature, where the activation heat no longer plays an important role, since it can take place in a binary collision, while a triple collision is required for the addition reaction².

II. Apparatus and Experimental Conditions

The effect of hydrogen and oxygen atoms at the temperature of liquid air and partly at -80°C as well on a number of substances is studied in the present paper. The apparatus employed has already been described in a paper on the production of H_2O_2 [1]. In a discharge arc, hydrogen was broken up into atoms (100%), as was oxygen (approximately 50%) at approximately 0.5 mm pressure (the flow rate in both cases was approximately 1 cc at/sec). The atoms traveled the shortest possible path into a reaction vessel 7 cm wide, cooled by liquid air. The test gases were conveyed through a vacuum mantle tube into the reaction chamber and mixed with the atoms only beneath the level of the liquid air. /1816

²Under the experimental conditions which we employed (0.5 mm pressure), only every 10^6 impact was a triple collision.

This made it possible to study the reaction with substances which no longer possess any vapor pressure at the temperature of liquid air. At the outlet of the vacuum mantle tube the substances were still gaseous; with the considerable excess of atoms in the inertialess reaction there was a greater probability of achieving a reaction than having them condense out, so that even compounds which have practically no vapor pressure at the temperature of liquid air can largely be made part of an addition compound.

In the tests with oxygen atoms it proved necessary to use liquid oxygen as a cooling bath. Liquid oxygen boils at 90° absolute, liquid air at approximately 83° abs. When working with liquid air, the oxygen atoms join with O_2 to form ozone, and it is naturally very troublesome and dangerous as well if the reaction product is mixed with liquid ozone. Raising the temperature to 90° absolute is sufficient to restrict formation of ozone. The reasons for this are as follows: the ozone vapor pressure is 0.015 mm at 83° abs. and 0.09 mm at 90° abs. On the one hand, this restricts condensation and on the other hand facilitates breakdown according to the reaction $O_3 + O = 2O_2$. We know from other experiments [4, 5] that the decomposition reaction $O_3 + O$ required an activation heat of 3 ± 1 kcal. From this we can readily calculate that under the experimental conditions employed the saturation pressure of O_3 at 83° abs will be crossed while this does not happen at 90° abs.

We know very little about the activation heats of addition reactions. Indeed, our tests do not provide the absolute values exactly; however, we can say that the activation heats for the addition, if the latter takes place with a significant yield, are very small inasmuch as it must concur with the recombination of the atoms and the condensation of the experimental gas, both of which reactions require no activation heat. This means that triple collisions are necessary for the addition reaction in general (even the recombination collisions on the wall are much more rare than the binary collisions of the homogeneous gas phase), so that during the experimental period only a limited number of such collisions (100) takes place, which is acceptable only with a lower activation heat for the addition reaction. Addition reactions, which proceed with a measurable yield at the temperature of liquid air, may have activation heat no higher than approximately 1 kcal if triple collision

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reactions are involved and no higher than 3 kcal if binary reactions are involved. Table I below gives a general idea of the dependence of the impact yield of any reaction with its activation heat Q and the reaction temperature T (abs). The given impact yields f were calculated from the relationship $f = a \cdot e^{-\frac{Q}{RT}}$ assuming that the (temperature-independent) steric factor of the reaction a possesses the largest possible value of 1.

TABLE I.

°C or T° absolute Impact yield of the reactions at an activation heat of

		100 cal	300 cal	1 kcal	3 kcal
-193	80	$10^{-0.274}$	$10^{-0.819}$	$10^{-2.74}$	$10^{-8.19}$
-183	90	$10^{-0.243}$	$10^{-0.729}$	$10^{-2.43}$	$10^{-7.29}$
-153	120	$10^{-0.182}$	$10^{-0.548}$	$10^{-1.82}$	$10^{-5.48}$
-80	193	$10^{-0.113}$	$10^{-0.340}$	$10^{-1.13}$	$10^{-3.40}$
+27	300	$10^{-0.073}$	$10^{-0.218}$	$10^{-0.73}$	$10^{-2.18}$

It must also be taken into account that the temperature in the interior of the reaction vessel, which has a diameter of 7 cm, is not precisely identical to the bath temperature. However, the latter, as similar experiments have shown, is only insignificantly higher (perhaps 10-20°) than the bath temperature, in the event that no rapidly proceeding reaction increases the temperature and only the recombination of atoms in triple collisions leads to a rise in temperature.

Intermediate compounds, which require an activation heat of more than 3 kcal for a destructive exchange reaction, are therefore protected from further attacks of the atoms at the temperature of liquid air, and inasmuch as they probably have no vapor pressure whatsoever at this temperature, they condense out. Although as condensation products they are in a permanent impact condition, as soon as they have once condensed out, experience indicates that they are resistant at low temperature almost without exception. As indicated by experiments at room temperature with hydrogen and oxygen atoms, the overwhelming majority of the exchange reactions that occur at room temperature proceed with an activation heat which is estimated as being more than 4 kcal, so that the temperature of the liquid air in all of these cases suppresses the decomposition reactions.

III. Experimental Results

The reaction products found were identified in most cases (1), to the extent that gases that would condense well at -190° were concerned, through a determination of the molecular weight ("vapor density"), saturation pressure, and in certain cases by determination of the melting point as well. (2) In many experiments, CO was burned to CO_2 on a platinum coil in a stream of oxygen. (3) The composition of organic compounds that are difficult to volatilize was determined by combustion analyses.

In the following, the data from one experiment only are given as an example of the reactions which were studied. (Gas volumes in cc of atmospheric pressure and 20°C).

a. Experiments with H-Atoms

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The reactions of H-atoms with oxygen, mercury and nitric oxide have already been described elsewhere [1, 2]. We should like to emphasize in particular here that oxygen and nitric oxide with an excess of H-atoms can be brought quantitatively to a reaction, since these two substances will not condense out under our experimental conditions. Since the other substances listed in Table II, which also react with H-atoms, no longer possess a vapor pressure at the temperature of liquid air, the reduced reaction capacity is partly evoked by the concurrence of condensation.

Prussic acid

The action of H-atoms on prussic acid at -190°C yields a product which begins to foam at approximately -60°C and changes to its stable components at room temperature. The chemical components include ammonia and a yellow oil in addition to a rather large amount of methylamine prussic acid, with the oil found to have the following composition according to two elementary analyses:

- | |
|--|
| 1) 44.01 % C, 8.05 % H, 39.10 % N
$\text{CH}_{1.92}\text{N}_{0.74}$, 0.13 H_2O , $\text{C}_4\text{H}_8\text{N}_3$, 0.5 H_2O . |
| 2) 39.31 % C, 8.31 % H, 30.50 % N
$\text{CH}_{1.72}\text{N}_{0.67}$, 0.39 H_2O . |

TABLE II.

Reaction of	Yield in % with	
	H-atoms at -190°	O-atoms at -183°
H ₂	—	0
O ₂	100	—
NO	100	10
Hg	70	Not studied
CO	0	1.3
SO ₂	80	8
N ₂ O	0	0
NH ₃	0	50
CH ₃ NH ₂	0	50
(CH ₃) ₃ N	Not studied	50
HCN	80	0
(CN) ₂	33	Not studied
HCl	Not studied	50
	(~0)	
C ₂ H ₂	< 2	55
C ₂ H ₄	33	67
C ₆ H ₆	17	20

In the second case the mixing ratio of active hydrogen (with approximately 1% H₂O) to prussic acid was approximately three times as great as in (1). The oily product (2) therefore contains more water, which apparently caused a more pronounced decomposition with NH₃ fission.

Experiments in which H-atoms acted upon methylamine under the same con- /1819
 ditions, had no result. Methylamine was obtained in a quantitatively pure condition. From this it follows that the ammonia and oil which were found cannot be a further product of hydration of the methylamine. The reaction product which is obtained at low temperature is apparently a uniform product to begin with, in which some unattacked prussic acid is included depending on the experimental conditions. It was found on the wall as a colorless and rather transparent coating. If we include all of the hydrogen in the calculation which was taken up by the prussic acid in the hydration process, we will have a gross composition of the original reaction product which corresponds rather exactly to CNH₃. This compound is not known and apparently not stable either, but rearranges itself when it melts, so that stronger and less strongly hydrated products result, e.g.,: 2CNH₃ = HCN + H₃C NH₂ (equation (1)). Molecular

hydrogen was not observed during decomposition. In the reaction of one liter = 1.12 g prussic acid, the reaction product was found to be 190 cc = 0.243 g methylamine, 92 cc = 0.065 g ammonia, and approximately 600 mg of the oily product, which had no further vapor pressure, and approximately 200 cc of re-formed or unattacked prussic acid. We see that methylamine and prussic acid occur almost exactly in the volume-ratio that would be predicted by equation (1). However, the quantitative analyses are carried out only with difficulty, since the resultant products are bases, which produce more or less readily dissociable salts with prussic acid.

Dicyan

Dicyan was attacked up to 1/3 and yielded approximately the same reaction products as prussic acid, but the identification was still significantly more difficult because the dicyan also yields condensation products.

The principal product is a dark reddish-brown solid reaction product which was almost equal on the basis of its characteristics to the condensation product from $2(\text{CN})_2$, 2NH_3 , hydrazulmine (theoretical composition: 34.74% C, 4.35% H, 60.95% N).

In its composition (43.34% C, 5.19% H, 43.2% N), on the other hand, it resembles the corresponding condensation product from methylamine and dicyan (theoretical composition: 43.35% C, 6.05% H, 50.60% N). The deviation from this value is probably due to a slight decomposition caused by the water mixed with the active hydrogen.

Example: 2,100 cc $(\text{CN})_2$ (= 4.50 g) with 3,720 cc of active hydrogen (hardly 2 H-atoms per $(\text{CN})_2$ per hour duration at 0.3 mm pressure and -190°C) yielded as the end product 1.45 g of solid reaction product $(2(\text{CN})_2, 2\text{CH}_3 \cdot \text{NH}_2) + 72 \text{ ccm } \text{NH}_3 + 24 \text{ ccm } \text{CH}_3 \cdot \text{NH}_2$.

Sulfur Dioxide

Sulfur dioxide also yields a reaction with H-atoms at low temperatures. From the total amount of hydrogen which is taken up, the product is obtained which has the same gross composition as H_2SO_2 . Following warming to room temperature, H_2S , SO_2 , water and sulfur were found. Since the precipitation

of sulfur took place in the reaction vessel even in those cases where the resulting gases were condensed out for analysis and were again vaporized, the appearance of SO can be predicted [6]. In the presence of H_2S and SO_2 , it would be hardly possible to carry out another proof. At -80° and room temperature, H_2S is produced from SO_2 and H-atoms in yields similar to those in the experiments at -190° , and sulfur is predipitated again when the condensed reaction products are warmed again.

From spectroscopic data [7] we are familiar with the binding strength of the second O-atom to SO_2 at 135 kcal. It follows that the assumed SO formation can take place not according to $\text{SO}_2 + \text{H} = \text{SO} + \text{OH} - 33$ kcal, but according to $\text{SO} + 2\text{H} = \text{SO} + \text{H}_2\text{O} + 83$ kcal. However, an activation heat of 1 kcal — a larger value would be expected due to the breakage of the O-bond — should suppress this triple collision reaction at -190° . It therefore seems to us to be unlikely that the stoichiometric composition of the original reaction product corresponding to H_2SO_2 is produced to a significant degree by a mixture of $\text{H}_2\text{O} + \text{SO}$. Any SO that appears must be due to decomposition of H_2SO_2 .

Example: 286 cc SO_2 (= 0.755 g) with 4,530 cc active hydrogen (approximately 15 H-atoms per SO_2) in one hour experimental time at 0.2 mm pressure and -190°C yields the following at the end products: 75.3 cc H_2S + 76.0 cc SO_2 + 190 mg (= 255 cc) H_2O + 110 mg (= 83.5 cc) S.

Ammonia, Nitrogen Protoxide, Methylamine

These materials form no addition with H-atoms and could be recovered quantitatively.

Benzene

Benzene yielded a hydration product which corresponds to a 17% dihydrobenzene on the basis of its combustion analysis. In the organic substances ethylene, acetylene and benzene, one can see in particularly simple form the influence of low temperatures on the chemical behavior or the H-atoms. At room temperature, Bonhoeffer and Hartek [8] found a violent effect of H-atoms on these compounds, with a large number of decomposition products with shortened carbon chains. Such products did not appear in our reactions, and if a chemical

reaction did occur, it was a hydrating one. In the hydration of the hydrocarbons which were added, one had the impression that the familiar stable chemical compounds were developed immediately, since the usual foaming or changing in the crystal structure was not observed when they were heated.

Ethylene

Ethylene yielded up to 33% ethane. Under our experimental conditions, it was possible with an excess of approximately 2 H-atoms per C_2H_4 per hour to reduce 400 cc out of 1,200 cc of ethylene to ethane.

Acetylene

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The detection of small amounts of ethylene in the hydration of acetylene was difficult to the extent that this substance still has a significant vapor pressure at the temperature of liquid air and does not differ very much from acetylene in its molecular weight. In any case, the hydrating effect of the H-atoms on the acetylene, if it took place at all, was very slight (less than 2%).

b. Experiments with O-Atoms

Ethylene

Ethylene yielded a colorless additive product which began to foam at -110° . Decomposition went to completion at room temperature. The reaction products that were observed included ethylene oxide, formaldehyde, acetaldehyde and carbon monoxide, as well as liquid aldehyde condensation products. The formation of ethylene oxide is expected and the mechanism of formation is obvious. It is worth noting the occurrence of acetaldehyde, since in this case a H-atom from one carbon must have migrated to another. Carbon monoxide and the other reaction products are formed in a significant secondary reaction of the additive products of the O-atoms which are initially formed.

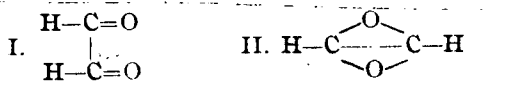
Example: In one hour, the following end products are obtained from 2,700 cc (= 3.12 g) C_2H_4 and 3,300 cc of active oxygen (scarcely one O-atom per C_2H_4) at 0.3 mm pressure and $-183^\circ C$: (900 cc C_2H_4) + 120 cc CO (produced at experimental temperature) + 30 cc CO (produced from decomposed reaction

products) + 126 cc H•CHO + 120 cc (CH₂)₂O + 385 cc CH₃•CHO + 725 mg of colorless -fluid aldehyde condensation products.

Acetylene

An unstable product was also obtained in the case of acetylene. At the temperature of liquid oxygen,,it initially appeared yellow to red in color and began to change to stable compounds at -90°. Carbon monoxide was given off in not insignificant quantities at the start. This carbon monoxide was produced to some extent even at the temperature of liquid air and could be captured by combustion and subsequent freezing out in the exhaust stream of oxygen, to be determined quantitatively later. No compound could be found in which one or two oxygen atoms were bound in the manner of ether. On the other hand, glyoxal could be found with a good yield in the reaction product (approximately 33 wt%). In addition, there were formic acid, not insignificant amounts of carbonic acid and a little water³. A migration of a H-atom must also have occurred in the formation of the formic acid. From the total oxidation of the acetylene it follows that two oxygen atoms are probably added per acetylene molecule, according to the following two possibilities:

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Compound 1 is the familiar glyoxal, compound 2 probably may not be stable at the temperature of liquid air and breaks down upon thawing at room temperature into the above-mentioned chemical compounds.

Example: In one hour the following were obtained from 550 cc (= 0.590 g) C₂H₂ and 3,300 cc active oxygen (approximately 4 O-atoms per C₂H₂) at 0.25 mm pressure and -183°C: 152 cc CO and a condensate which yielded with slow heating to approximately -90°C the following: 7.2 cc CO + 78 cc CO₂ + 245 cc C₂H₂, and

³These stable reaction products (glyoxal, formic acid, CO, CO₂, H₂O) were also obtained in the combustion of acetylene as intermediate products; cf. also [9, 10, 11].

further heating to room temperature yielded the following: 5 cc CO + 25 cc CO₂ + 10 cc C₂H₂. The residue was 78 mg (= 108 cc) H₂O + 220 mg (= 115 cc) H•COOH + 207 mg (CHO)₂, 1/2 H₂O.

The warming of the reaction vessel from -95° to -90° proceeded very slowly (one hour), with simultaneous irrigation of the reaction vessel with hydrogen. The fact that further heating of the reaction product still continued to yield acetylene and CO₂ can probably be interpreted only as being due to a decomposition process (possibly a strong adsorption).

Carbon Monoxide and Sulfur Dioxide

Carbon monoxide yields approximately 1.3% carbonic acid. It is noteworthy that this compound is not created rapidly by the addition of O-atoms. Hardeck and Kopsch [12] have observed that there is only a slight influence of O-atoms at room temperature.

In one hour, 1,500 cc CO with 2 O-atoms per CO at 0.4 mm and -183°C yielded 20 cc of CO₂.

In addition, SO₂ adds O-atoms with formation of sulfur trioxide at only a moderate rate (8%), forming sulfuric acid with water and determined as barium sulfate.

In one hour, 190 cc of SO₂ with a 15-fold excess of O-atoms at 0.3 mm pressure and -183°C yielded 17.5 cc of SO₃.

Nitric oxide yielded only small amounts of NO₂ and it is still indefinite whether the atomic oxygen is responsible, since the NO₂ formation proceeds at low temperatures even under the influence of molecular oxygen.

No additive products could be found in the case of prussic acid, nitrogen protoxide and hydrogen.

Hydrochloric Acid

Hydrochloric acid was attacked by O-atoms approximately 50%. Water and chlorine were the principal products. Five percent of the added HCl was retained as ClO₂, determined through observation of the absorption spectrum as well as by titration. This finding indicates, even in the case of the formation of an

unstable additive product, that some HClO can be assumed to have been present. /1823
Likewise the chlorine dioxide could have developed from primarily formed chlorine atoms (possibly via ClO).

In one hour, 280 cc of Cl_2 + 55 cc ClO_2 + 580 cc H_2O were formed from 1,090 cc of HCl gas with 3,300 cc of active oxygen (two O-atoms per HCl).

Ammonia, Methylamine, Trimethylamine

All three substances add O-atoms with a good yield (~50%). Intensively yellow-colored compounds result which decompose at approximately -80° with melting and violent foaming. A thorough analysis of the resultant products was not carried out inasmuch as the latter react with each other and with the unconsumed raw material to a significant degree with formation of nonvolatile compounds. Thus, the principal product from NH_3 is a white solid salt $(\text{NH}_4)_2\text{N}_2\text{O}_2$, while CH_3NH_2 yields a slightly colored paste that later turns brown (in a vacuum), which reduced an ammoniacal silver solution, and trimethylamine yielded a brownish oil. The decomposition product of methylamine oxide included ammonia (6%) and nitric oxide, while trimethylamine oxide yielded formaldehyde among other substances. The two amines at the temperature of liquid oxygen yielded volatile carbon and hydrogen compounds (CO , C_2H_4 , CH_4 , H_2), which burns in the exhaust stream of O_2 and were found as CO_2 and H_2O . Small local explosions occurred on some occasions during the experiments with trimethylamine.

Benzene

The addition reaction of O-atoms in benzene was studied to a somewhat greater degree (Table III). If the reaction vessel was cooled with liquid O_2 as usual, only a small amount of benzene was converted (10%). At this temperature, the reaction product initially had only a dirty yellow color, there was no foaming during heating, but the formation of an intensively colored red compound (light absorption between 5,450 and 5,650Å) was found. The eventually remaining reddish-brown sticky-solid reaction product in one case had a composition of 48.77% C, 5.57% H = $\text{C}_6\text{H}_6\text{O}_{3.15}$, 1.08 H_2O .

TABLE III. BENZENE + O-ATOM.

No.	°C	Width of reaction vessel in mm	Raw materials in millimoles/min		Pressure mm Hg	Final products millimoles/minute				Mg/min solid reaction product	Yield, mg solid per per mil- limole C_6H_6	Notes	Nr.
			O_2 acti- vated	C_6H_6		Created at exper- imental temp.		Created from the decayed reaction product					
						CO	CO_2	CO	CO_2				
1	-183	35	0.58	0.362	0.09	0.0015	0.002	0.0015	—	0.327	0.90		
2	-183	70	2.3	0.273	0.3	0.016	0.038	0.007	—	4.38	16.0	$C_6H_6O_{3.16}$, 1.08 H_2O	2
3	-80	35	0.58	0.320	0.09	0.133*)			0.0028	3.8	11.9		
4	-80	35	2.3	0.435	0.28	0.172*)		0.0027	0.0041	13.4	30.8	57% benzene retained	4
5	-80	35	2.3	0.343	0.4			0.003		15.0	43.7	$C_6H_6O_{3.55}$, 0.26 H_2O	5
6	-80	35	7.4	0.437	0.45			0.003		25.1	57.5		
7	-80	70	7.4	0.347	0.45			0.000		18.0	51.9	No benzene left unattacked	7

*The CO_2 created by the reaction (at $-80^\circ C$) and from CO by combustion on the Pt-coil was not captured separately but determined jointly.

If the reaction vessel was only cooled to -80° (versions No. 3-7), much higher benzene yields were obtained (up to 100%). The colorless glassy reaction product that was obtained at -80° began to decompose only at -30° with foaming. The intermediate product broke down as follows: 2% CO_2 , 1% CO, 10% $H\cdot COOH$ and H_2O . The remaining solid product was initially completely colorless, but soon took on a yellow color that changed to red.

Combustion yielded the following: 51.7% C, 4.71% H or $C_6H_6O_{3.55}$, 0.26 H_2O .

The oxygen was partly bound in the quinones (approximately 10%), since the fresh reaction product turned acid potassium iodide solution blue.

Possibly it consists partly of the o-quinone described by Willstaetter [13], which can be obtained only at low temperature in a colorless modification which spontaneously turns to red.

The work of A. v. Antropoff, Weil and Fraunhofer [14] on the determination of noble gas compounds led us to try to determine whether it might be possible to add oxygen atoms to xenon. For this purpose, a discharge was created in a mixture of oxygen and xenon (approximately 1 mm partial pressure) and the discharge tube was cooled at one point with liquid oxygen or with liquid methane. The discharged tube was fitted with aluminum electrodes and was ignited for many hours so that the oxygen pressure remained constant within 1% for one hour. The saturation pressure of the xenon was 0.2 mm at -183° and 2.0 mm at -164° ; hence, a greater portion of the xenon was condensed out at the temperature of boiling oxygen. The discharge not only split the oxygen but also excited the xenon (emission of its line spectrum), and we noted the appearance of the metastable xenon atom as being especially favorable for a valence activation and an occasional formation of XeO , which is supposed to have no measurable vapor pressure at the temperature of liquid oxygen. However, we did not observe even the slightest drop in pressure of oxygen during the discharge process, so that the demonstrability of the existence of xenon oxide was zero.

Summary

From the factual material presented herein, it can be concluded that in general those addition reactions proceed with difficulty in which another stable compound is created from a stable chemical compound through increasing the valence of an atom. On the other hand, at low temperatures those compounds show preferential addition in which a secondary valence is created chemically. This gives rise to a chemical bond that is so weak that the compounds that result at room temperature are no longer found. Such intermediate compounds might perhaps be expected from the standpoint of the London theory which showed that when two atoms or molecules approach one another, potential holes of shallow depth (corresponding to our unstable products) must be traversed before the most stable arrangement is achieved. It is only as a result of this proportionation or rearrangement of these unstable intermediate compounds that the familiar final compounds can be obtained. The stoichiometric compositions of the probable intermediate compounds described in this paper could not be termed as proven, but it would probably be very difficult to explain the phenomena

that were observed without assuming that such intermediate compounds did exist. In order to obtain more precise knowledge concerning the conversion or addition that takes place at low temperatures, the intermediate stages must be subjected to a systematic x-ray study. Further studies in this direction are planned.

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